

AMINE-BOOSTED DETERGENT

TECHNICAL FIELD

[001] This disclosure relates to detergent additive compositions. More particularly, this disclosure describes amine-boosted detergent compositions and lubricating oil compositions containing the same.

BACKGROUND

[002] Metal detergent additives are often used in automotive lubricants to provide important benefits such as preventing deposit formation and increasing fuel economy.

[003] In particular, overbasing a detergent can provide a metal base reserve which neutralizes corrosive acids that are generated in an engine environment. For calcium detergents, the degree to which the detergent has been overbased depends on the level of calcium carbonate (CaCO_3) present.

[004] Overbased calcium metal detergents are oil-soluble particles that have a surfactant outer shell and a calcium carbonate core. The degree of overbasing is indicated by the Total Base Number (TBN). In general, a higher TBN increases the operating period under harsh conditions before the lubricant needs to be replaced.

[005] One drawback of these types of detergents is that the presence of metals leads to sulfated ash which can poison exhaust gas treatment catalysts. While calcium carbonate contributes to the TBN, it can also lead to the production of sulfated ash. One approach to this problem is to limit the metal content of additive packages.

SUMMARY

[006] In one aspect, there is provided a process for preparing a low ash detergent, the process comprising: mixing a surfactant composition that includes a hydroxybenzoate, sulfonate, or phosphonate detergent with an ashless nitrogen-

containing compound to boost the base number of the hydroxybenzoate, sulfonate or phosphonate detergent.

[007] In another aspect, there is provided a process for preparing a low ash detergent, the process comprising: mixing hydroxybenzoate, sulfonate, or phosphonate detergent with an amine or amine derivative, wherein the amine or amine derivative is added to overbase or boost the base number of the hydroxybenzoate, sulfonate or phosphonate detergent.

[008] In yet another aspect, there is provided a lubricating oil composition comprising: major amount of an oil of lubricating viscosity; and minor amount of a low ash detergent made from a process comprising: mixing hydroxybenzoate, sulfonate, or phosphonate detergent with an amine or amine derivative, wherein the amine or amine derivative is added to overbase or boost the base number of the hydroxybenzoate, sulfonate or phosphonate detergent.

DETAILED DESCRIPTION

[009] In this specification, the following words and expressions, if and when used, have the meanings ascribed below.

[010] The term "alkyl" or related term refers to saturated hydrocarbon groups, which can be linear, branched, cyclic, or a combination of cyclic, linear and/or branched. The term "alkenyl" or related term refers to unsaturated hydrocarbon groups, which can be linear, branched, cyclic, or a combination of cyclic, linear and/or branched.

[011] In the context of hydrocarbon-based formulations (particularly lubricants), the term "ash" or related term refers to metallic compounds remaining after hydrocarbons have been calcinated. This ash is mainly derived from chemicals used in certain additives, as well as solids. The term "sulfated ash" refers to a product of combustion of metals commonly found in detergents. As a lubricant property, sulfated ash content is a measure of metal content (usually Zn, Ca, and Mg).

[012] The term “ashless” or related term refers to formulations or additives that do not generate ash or limit generation of ash. Ashless additives are generally free of metals (including boron), silicon, halogen, or contain these elements in concentrations below typical instrument detection limits.

[013] A “minor amount” or related term means less than 50 wt % of a composition, expressed in respect of the stated additive and in respect of the total weight of the composition, reckoned as active ingredient of the additive.

[014] A “major amount” or related term means an amount greater than 50 wt % based on the total weight of the composition.

[015] The term “lime” refers to calcium hydroxide also known as slaked lime or hydrated lime.

[016] The term “Total Base Number” or “TBN” refers to the level of alkalinity in an oil sample, which indicates the ability of the composition to continue to neutralize corrosive acids, in accordance with ASTM Standard No. D2896 or equivalent procedure. The test measures the change in electrical conductivity and the results are expressed as mg KOH/g (the equivalent number of milligrams of KOH needed to neutralize 1 gram of a product). Therefore, a high TBN reflects strongly overbased products and, as a result, a higher base reserve for neutralizing acids.

[017] The present invention describes a low ash detergent that results in lower production of sulfated ash per base number (BN) compared to a conventionally overbased detergent when used as an additive in a lubricating oil under engine operating conditions. The low ash detergent of the present invention comprises: 1) a surfactant and 2) a nitrogen-containing compound. The nitrogen-containing compound such as an amine or amine-derivative is used to overbase the detergent and boost the TBN. In one aspect, present invention is related to an amine-boosted detergent wherein the nitrogen-containing compound is an amine or amine derivative. In another aspect, the nitrogen-containing compound is ashless.

[018] The low ash detergents of the present invention generally contain less metal salts compared to a conventional detergent which heavily relies on metal salts

(e.g., CaCO_3) to neutralize acids during engine operation. Consequently, the detergents of the present invention generate less sulfated ash. The nitrogen-containing compounds contribute to the total base number but do not contribute to the production of sulfated ash.

[019] Particularly useful surfactants compatible with the present invention include metal detergents such as salts of hydroxybenzoate, sulfonate, and phosphonate. Some non-limiting examples of compatible metal detergents include alkyl or alkenyl aromatic sulfonates, borated sulfonates, sulfurized or unsulfurized metal salts of multi hydroxy alkyl or alkenyl aromatic compounds, metal salts of alkyl or alkenyl hydroxybenzoic acid, alkyl or alkenyl hydroxy aromatic sulfonates, sulfurized or unsulfurized alkyl or alkenyl naphthenates, metal salts of alkanolic acids, metal salts of an alkyl or alkenyl multiacid, and chemical and physical mixtures thereof. Other non-limiting examples of suitable metal detergents include salicylates, thiophosphonates and the like. Non-limiting examples of suitable metals include alkali metals, alkaline metals and transition metals. In some embodiments, the metal is Ca, Mg, Ba, K, Na, Li or the like.

[020] Particularly useful nitrogen-containing compounds compatible with the present invention include amines and amine derivatives such as carbamates, ureas, amides, and imides. The nitrogen-containing compounds may contain heteroatoms (e.g., alcohols), saturated groups, aromatic groups, and the like.

[021] Examples of amines or amine-derivatives include alkylated amine (e.g., 2-ethylhexyl(tallow)methylamine, ethyl hexyl amine, octylamine), hydrocarbyl amine, ethylene diamine, N-methylethanolamine, 1,1,-dimethylethylenediamine, 2-methoxyethylamine, ethanolamine (e.g., di-ethanolamine), N-methylpropylenediamine, piperazine (e.g., dodecylpiperazine), urea, tetramethylurea, diphenylamine, alkylated diphenylamine, benzyl amine, N-phenyl phenylenediamine, tri-ethylene tetra-amine, tri-ethanol-amine, 1,4-diazabicyclo[2.2.2]octane, N,N'-bis(3-aminopropyl)ethylenediamine ("N4 amine"), phenoxy amine (e.g., 2-phenoxyethylamine, C20-C24 alkyl-2-phenoxyethylamine), 2-(2-aminoethoxy)

naphthalene, N-(3-(dimethyl amino) propyl) benzamide, phenylamine (e.g., 3-phenylpropylamine), benzamide, amino acid, and phthalimide.

[022] More specifically, suitable phthalimides include N-(2-hydroxyethyl)phthalimide, N-(2-aminoethyl)phthalimide, N-(3-hydroxypropyl)phthalimide, N-(3-aminopropyl) phthalimide, N-(2-(methylamino)ethyl) phthalimide, N-(3-(methylamino)propyl) phthalimide, N-(2-(dimethylamino)ethyl) phthalimide, and N-(3-(dimethylamino)propyl) phthalimide.

[023] In some embodiments, the low ash detergent of the present invention may include a mixture of nitrogen-containing compounds such as an amine and a carbamate.

Detergent Synthesis

[024] The low ash detergents of the present invention may be synthesized by any compatible method. However, one advantage is that the manufacture of the low ash detergents of the present invention is generally compatible with conventional detergent manufacturing process such as the following. For example, the manufacture of conventional overbased calcium alkylhydroxybenzoate detergent often begins by reacting alkylphenol with a metal base. The product is then carboxylated (i.e., treated with CO₂) and acidified. The resulting acid product can be neutralized by lime and overbased. Some of these steps (e.g., the second neutralization and overbasing) can proceed concurrently. A more detailed description of this process can be found in US 8,030,258, which is hereby incorporated by reference.

[025] The detergents of the present invention may be synthesized using any compatible method. In one aspect, synthesis of the detergent of the present invention differs from synthesis of a conventional detergent in that the low ash detergent of the present invention is boosted with a nitrogen-containing compound (e.g., amine or amine-derivative) instead of a metal base (e.g., calcium carbonate).

[026] As an illustrative example, the process for preparing an overbased amine-boosted alkaline earth metal alkylarylsulfonate includes: (a) neutralizing an alkyl toluene/benzene sulfonic acid an alkaline earth metal base (e.g., MgO) to form an

alkaline earth metal alkyl toluene/benzene sulfonate; (b) contacting the alkaline earth metal alkyl toluene/benzene sulfonate and the alkaline earth metal base from step (a) with at least one carboxylic acid having from about one to four carbon atoms to form a mixture of alkaline earth metal alkylarylsulfonate and at least one alkaline earth metal carboxylic acid salt; and (c) overbasing the alkaline earth metal alkylarylsulfonate from step (b) with an amine or amine derivative, and at least one acidic overbasing material in the presence of the at least one alkaline earth metal carboxylic acid salt from step (b). A more detailed description of making the alkaline earth metal alkylarylsulfonate can be found in US 6,479,440, which is hereby incorporated by reference.

[027] As an illustrative example, the process for preparing an overbased amine-boosted alkaline earth metal alkylarylsulfonate includes: (a) neutralizing an alkyl toluene/benzene sulfonic acid an alkaline earth metal base (e.g., CaO or Ca(OH)₂) to form an alkaline earth metal alkyl toluene/benzene sulfonate; and (b) overbasing the alkaline earth metal alkylarylsulfonate from step (a) with an amine or amine derivative. A more detailed description of making the alkaline earth metal alkylarylsulfonate can be found in U.S. Pat. No. 8,076,272, which is hereby incorporated by reference.

[028] As an illustrative example, the process for preparing an overbased amine-boosted alkaline earth metal alkylhydroxybenzoate includes: (a) reacting alkylphenol with an alkali metal base to produce an alkali metal alkylphenate; (b) carboxylating the alkali metal alkylphenate obtained in step (a) with carbon dioxide so that at least 50 mole % of the starting alkylphenol has been converted to an alkali metal alkylhydroxybenzoate; (c) acidifying the alkali metal alkylhydroxybenzoate obtained in step (b) with an aqueous solution of a strong acid to produce an alkylhydroxybenzoic acid; (d) neutralizing the alkylhydroxybenzoic acid from step (c) with a molar excess of an alkaline earth metal base and at least one solvent from the following: aromatic hydrocarbons, aliphatic hydrocarbons; monoalcohols, and mixtures thereof to form an alkaline earth metal alkylhydroxybenzoate; (e) contacting the alkaline earth metal alkylhydroxybenzoate and alkaline earth metal base from step d) with at least one carboxylic acid having from about one to four carbon atoms in the

presence of a solvent (i.e., aromatic hydrocarbons, aliphatic hydrocarbons, monoalcohols, or mixtures thereof) to form a mixture of alkaline earth metal alkylhydroxybenzoate and at least one alkaline earth metal carboxylic acid salt; and (f) overbasing the alkaline earth metal alkylhydroxybenzoate from step e) with an amine, or amine derivative and at least one acidic overbasing material in the presence of the at least one alkaline earth metal carboxylic acid salt from step (e) and a solvent (i.e., aromatic hydrocarbons, aliphatic hydrocarbons, monoalcohols, or mixtures thereof).

[029] In another embodiment, the amine can be added during neutralization before the overbasing step.

[030] It is understood that the specific order of one or more steps in the detergent (e.g., alkylarylsulfonate, alkylhydroxybenzoate, etc.) synthesis pathway may be reordered, combined, or slightly modified as desired as long as it is compatible and in accordance with the present invention. For illustration purposes, the following embodiments are provided for detergent synthesis involving alkylhydroxybenzoic acid, alkyl aromatic sulfonic acid, and alkenyl aromatic sulfonic acid. These changes may also be applied to other detergent synthesis pathways compatible with the present invention.

[031] For example, in the alkylhydroxybenzoate detergent synthesis pathway, the alkylhydroxybenzoic acid may be neutralized by a lime slurry (i.e., $\text{Ca}(\text{OH})_2$). Optionally, an amine may be present in the lime slurry during the neutralization step. The lime slurry and an amine or amine derivative can be charged into a reactor with both reacting together with CO_2 .

[032] According to an embodiment, the amine treatment can be performed after the alkylhydroxybenzoic acid has been neutralized by the lime slurry and after excess lime has reacted with CO_2 to form metal carbonate (e.g., calcium carbonate).

[033] According to an embodiment the amine treatment can be performed after the alkylhydroxybenzoic acid has been neutralized by the lime slurry and before the lime slurry has reacted with CO_2 .

[034] According to an embodiment, the amine can be charged to the reactor after the alkylhydroxybenzoic acid has been neutralized with the lime slurry. The amine or amine derivative may be dispersed by the neutralized surfactant without further treatment.

[035] According to an embodiment, the alkylhydroxybenzoic acid can be neutralized by the amine which is in excess versus the quantity required to neutralize the alkylhydroxybenzoic acid. The excess amine can react with CO_2 to form a carbamate.

[036] According to an embodiment, the alkylhydroxybenzoic acid can be neutralized by the amine which is in excess versus the quantity required to neutralize the alkylhydroxybenzoic acid.

[037] According to an embodiment, the alkylhydroxybenzoic acid can be neutralized by the lime slurry and then the amine is treated with ethylene carbonate. In some embodiments, a metal base besides lime or in addition to lime may be used. Suitable metal bases include alkali and alkali earth metal bases. An example of suitable metal base includes MgO and the like.

[038] According to an embodiment, in the alkyl or alkenyl aromatic sulfonates detergent synthesis pathway, the alkyl or alkenyl aromatic sulfonic acid may be neutralized by a lime slurry (i.e., $\text{Ca}(\text{OH})_2$). Optionally, an amine may be present in the lime slurry during the neutralization step. The lime slurry and an amine or amine derivative can be charged into a reactor with both reacting together with CO_2 .

[039] According to an embodiment, the amine treatment can be performed after the alkyl or alkenyl aromatic sulfonic acid has been neutralized by the lime slurry and after excess lime has reacted with CO_2 to form metal carbonate (e.g., calcium carbonate).

[040] According to an embodiment the amine treatment can be performed after the alkyl or alkenyl aromatic sulfonic acid has been neutralized by the lime slurry and before the lime slurry has reacted with CO_2 .

[041] According to an embodiment, the amine can be charged to the reactor after the alkyl or alkenyl aromatic sulfonic acid has been neutralized with the lime slurry. The amine or amine derivative may be dispersed by the neutralized surfactant without further treatment.

[042] According to an embodiment, the alkyl or alkenyl aromatic sulfonic acid can be neutralized by the amine which is in excess versus the quantity required to neutralize the alkyl or alkenyl aromatic sulfonic acid. The excess amine can react with CO₂ to form a carbamate.

[043] According to an embodiment, the alkyl or alkenyl aromatic sulfonic acid can be neutralized by the amine which is in excess versus the quantity required to neutralize the alkyl or alkenyl aromatic sulfonic acid.

[044] According to an embodiment, the alkyl or alkenyl aromatic sulfonic acid can be neutralized by the lime slurry and then the amine is treated with ethylene carbonate. In some embodiments, a metal base besides lime or in addition to lime may be used. Suitable metal base include alkali and alkali earth metal bases. An example of suitable metal base includes MgO and the like.

[045] The product of amine treatment includes ammonium carbamate and calcium carbonate. The latter is produced in a reduced amount compared to manufacture or synthesis of a conventional detergent.

[046] Any amine or amine-derivative reagent compatible with the present invention may be used. These amines include, for example, primary, secondary, and tertiary amines and derivatives thereof. The amines may contain heteroatoms (e.g., alcohols), saturated groups, aromatic groups, and the like.

[047] Compatible primary amines or amine-derivatives include, for example, glycine, 2-ethylhexylamine, octylamine, 2-methoxyethylamine, 2-phenoxyethylamine, 2-(2-aminoethoxy) naphthalene, 3-phenylpropylamine, benzamide, and the like.

[048] Compatible secondary amines or amine-derivatives include, for example, ethylene diamine, diphenyl amine, alkylated diphenyl amine, tri-ethylene tetra-amine,

N phenyl phenylene diamine, N-ethyl butylamine, iso-propyl methylamine, N-ethylhexylamine, N-methylethanolamine, di-ethanolamine, phthalimide, and the like.

[049] Compatible tertiary amines or amine-derivative include, for example, tri-ethanol amine, 1,4-diazabicyclo[2.2.2]octane, dialkylpiperazine, 2-ethylhexyl(tallow)methylamine, tetramethylurea, and the like.

[050] Some amines or amine-derivatives may have multiple amines or amine-derivatives that are independently primary, secondary, or tertiary amines. Examples include 1,1,-dimethylethylenediamine, N-methylpropylenediamine, 1-dodecylpiperazine, N,N'-bis(3-aminopropyl)ethylenediamine ("N4 amine"), N-(3-(dimethyl amino) propyl) benzamide, and the like.

[051] The amine treatment utilizes one or more solvents during the amine treatment step. Suitable solvents include xylene, toluene, methanol, and the like.

[052] The alkyl or alkenyl group of the amine-boosted alkaline earth metal alkylhydroxybenzoate, or alkylarylsulfonate can be derived from an alkyl substituent with C10-40 alkyl groups, preferably C12-C30, C14-C18, C18-30, C20-28, C20-24 or mixtures thereof.

[053] In one embodiment, the alkyl substituent is a residue derived from an alpha-olefin having from 14 to 28 carbon atoms per molecule. In one embodiment, the alkyl substituent is a residue derived from an alpha-olefin having from 14 to 18 carbon atoms per molecule. In one embodiment, the alkyl substituent is a residue derived from an alpha-olefin having from 20 to 28 carbon atoms per molecule. In one embodiment, the alkyl substituent is a residue derived from an alpha-olefin having from 20 to 24 carbon atoms per molecule. In one embodiment, the alkyl substituent is a residue derived from an olefin comprising C12 to C40 oligomers of a monomer selected from propylene, butylene, or mixtures thereof. Examples of such olefins include propylene tetramer, butylene trimer, isobutylene oligomers, and the like.

[054] The olefins employed may be linear, isomerized linear, branched or partially branched linear. The olefin may be a mixture of linear olefins, a mixture of isomerized linear olefins, a mixture of branched olefins, a mixture of partially branched

linear or a mixture of any of the foregoing. The alpha-olefin may be a normal alpha-olefin, an isomerized normal alpha-olefin, or a mixture thereof.

[055] In one embodiment where the alkyl substituent is a residue derived from an isomerized alpha-olefin, the alpha-olefin can have an isomerization level (I) of 0.1 to 0.4 (e.g., 0.1 to 0.3, or 0.1 to 0.2). The isomerization level (I) can be determined by ^1H NMR spectroscopy and represents the relative amount of methyl groups ($-\text{CH}_3$) (chemical shift 0.30-1.01 ppm) attached to the methylene backbone groups ($-\text{CH}_2-$) (chemical shift 1.01-1.38 ppm) and is defined by the following formula:

$$I = m / (m + n)$$

where m is the ^1H NMR integral for methyl groups with chemical shifts between 0.30 ± 0.03 to 1.01 ± 0.03 ppm, and n is the ^1H NMR integral for methylene groups with chemical shifts between 1.01 ± 0.03 to 1.38 ± 0.10 ppm.

[056] The amine-boosted alkaline earth metal alkylhydroxybenzoate of the present disclosure has a TBN, on an actives basis, of 90 to 600 mg KOH/g such as 90 to 500 mg KOH/g, 90 to 450 mg KOH/g, or 90 to 400 mg KOH/g, 90 to 350 mg KOH/g, 90 to 300 mg KOH/g, 150 to 590 mg KOH/g, 150 to 500 mg KOH/g, 150 to 450 mg KOH/g, 150 to 400 mg KOH/g, 150 to 350 mg KOH/g, 150 to 300 mg KOH/g, 200 to 590 mg KOH/g, 200 to 500 mg KOH/g, 200 to 450 mg KOH/g, 200 to 400 mg KOH/g, or 200 to 350 mg KOH/g.

[057] The amine-boosted alkaline earth metal alkylarylsulfonate of the present disclosure has a TBN, on an actives basis, of 20 to 700 mg KOH/g such as 20 to 650 mg KOH/g, 20 to 600 mg KOH/g, 20 to 550 mg KOH/g, 20 to 500 mg KOH/g, 150 to 700 mg KOH/g, 150 to 650 mg KOH/g, 150 to 600 mg KOH/g, 150 to 550 mg KOH/g, 150 to 500 mg KOH/g, 200 to 700 mg KOH/g, 250 to 700 mg KOH/g, 300 to 700 mg KOH/g, 200 to 600 mg KOH/g, 250 to 550 mg KOH/g, 300 to 500 mg KOH/g, or 350 to 450 mg KOH/g.

[058] In another embodiment, the amine boosted alkaline earth metal detergent comprises more than one surfactant, often known in the art as complex or hybrid detergent. For example, the amine-boosted overbased alkaline earth metal

detergent comprises both alkylhydroxybenzoate and alkylarylsulfonate in the surfactant system.

Lubricating Oil Compositions

[059] The detergent compositions of present disclosure may be used in lubricating oil. When employed in this manner, the detergent is usually present in the lubricating oil composition in concentrations ranging from 0.05 wt % to 10 wt % (including, but not limited to, 0.1 to 5 wt %, 0.2 to 4 wt %, 0.5 to 3 wt %, 1 to 2 wt %, and so forth), based on the total weight of the lubricating oil composition. If other detergents are present in the lubricating oil composition, a lesser amount of the detergent of the present invention may be used.

[060] Oils used as the base oil will be selected or blended depending on the desired end use and the additives in the finished oil to give the desired grade of engine oil, e.g. a lubricating oil composition having an Society of Automotive Engineers (SAE) Viscosity Grade of 0W, 0W-8, 0W-16, 0W-20, 0W-30, 0W-40, 0W-50, 0W-60, 5W, 5W-20, 5W-30, 5W-40, 5W-50, 5W-60, 10W, 10W-20, 10W-30, 10W-40, 10W-50, 15W, 15W-20, 15W-30, or 15W-40.

[061] The oil of lubricating viscosity (sometimes referred to as "base stock" or "base oil") is the primary liquid constituent of a lubricant, into which additives and possibly other oils are blended, for example to produce a final lubricant (or lubricant composition). A base oil, which is useful for making concentrates as well as for making lubricating oil compositions therefrom, may be selected from natural (vegetable, animal or mineral) and synthetic lubricating oils and mixtures thereof.

[062] Definitions for the base stocks and base oils in this disclosure are the same as those found in American Petroleum Institute (API) Publication 1509 Annex E ("API Base Oil Interchangeability Guidelines for Passenger Car Motor Oils and Diesel Engine Oils," December 2016). Group I base stocks contain less than 90% saturates and/or greater than 0.03% sulfur and have a viscosity index greater than or equal to 80 and less than 120 using the test methods specified in Table E-1. Group II base stocks contain greater than or equal to 90% saturates and less than or equal to 0.03%

sulfur and have a viscosity index greater than or equal to 80 and less than 120 using the test methods specified in Table E-1. Group III base stocks contain greater than or equal to 90% saturates and less than or equal to 0.03% sulfur and have a viscosity index greater than or equal to 120 using the test methods specified in Table E-1. Group IV base stocks are polyalphaolefins (PAO). Group V base stocks include all other base stocks not included in Group I, II, III, or IV.

[063] Natural oils include animal oils, vegetable oils (e.g., castor oil and lard oil), and mineral oils. Animal and vegetable oils possessing favorable thermal oxidative stability can be used. Of the natural oils, mineral oils are preferred. Mineral oils vary widely as to their crude source, for example, as to whether they are paraffinic, naphthenic, or mixed paraffinic-naphthenic. Oils derived from coal or shale are also useful. Natural oils vary also as to the method used for their production and purification, for example, their distillation range and whether they are straight run or cracked, hydrorefined, or solvent extracted.

[064] Synthetic oils include hydrocarbon oil. Hydrocarbon oils include oils such as polymerized and interpolymerized olefins (e.g., polybutylenes, polypropylenes, propylene isobutylene copolymers, ethylene-olefin copolymers, and ethylene-alphaolefin copolymers). Polyalphaolefin (PAO) oil base stocks are commonly used synthetic hydrocarbon oil. By way of example, PAOs derived from C₈ to C₁₄ olefins, e.g., C₈, C₁₀, C₁₂, C₁₄ olefins or mixtures thereof, may be utilized.

[065] Other useful fluids for use as base oils include non-conventional or unconventional base stocks that have been processed, preferably catalytically, or synthesized to provide high performance characteristics.

[066] Non-conventional or unconventional base stocks/base oils include one or more of a mixture of base stock(s) derived from one or more Gas-to-Liquids (GTL) materials, as well as isomerase/isodewaxase base stock(s) derived from natural wax or waxy feeds, mineral and or non-mineral oil waxy feed stocks such as slack waxes, natural waxes, and waxy stocks such as gas oils, waxy fuels hydrocracker bottoms, waxy raffinate, hydrocrackate, thermal crackates, or other mineral, mineral oil, or even non-

petroleum oil derived waxy materials such as waxy materials received from coal liquefaction or shale oil, and mixtures of such base stocks.

[067] Base oils for use in the lubricating oil compositions of present disclosure are any of the variety of oils corresponding to API Group I, Group II, Group III, Group IV, and Group V oils, and mixtures thereof, preferably API Group II, Group III, Group IV, and Group V oils, and mixtures thereof, more preferably the Group III to Group V base oils due to their exceptional volatility, stability, viscometric and cleanliness features.

[068] Typically, the base oil will have a kinematic viscosity at 100°C (ASTM D445) in a range of 2.5 to 20 mm²/s (e.g., 3 to 12 mm²/s, 4 to 10 mm²/s, or 4.5 to 8 mm²/s).

[069] The present lubricating oil compositions may also contain conventional lubricant additives for imparting auxiliary functions to give a finished lubricating oil composition in which these additives are dispersed or dissolved. For example, the lubricating oil compositions can be blended with antioxidants, ashless dispersants, anti-wear agents, detergents, rust inhibitors, dehazing agents, demulsifying agents, friction modifiers, metal deactivating agents, pour point depressants, viscosity modifiers, antifoaming agents, co-solvents, package compatibilizers, corrosion-inhibitors, dyes, extreme pressure agents and the like and mixtures thereof. A variety of the additives are known and commercially available. These additives, or their analogous compounds, can be employed for the preparation of the lubricating oil compositions of the invention by the usual blending procedures.

[070] Each of the foregoing additives, when used, is used at a functionally effective amount to impart the desired properties to the lubricant. Thus, for example, if an additive is an ashless dispersant, a functionally effective amount of this ashless dispersant would be an amount sufficient to impart the desired dispersancy characteristics to the lubricant. Generally, the concentration of each of these additives, when used, may range, unless otherwise specified, from about 0.001 to about 20 wt %, such as about 0.01 to about 10 wt %.

[071] The following illustrative examples are intended to be non-limiting.

EXAMPLES

[072] Examples provide low ash detergents synthesized from alkylhydroxy benzoate or sulfonate compositions. The reactions were carried out in a 5 liters four-neck glass reactor equipped with heating and cooling capability and fitted with a stainless steel mechanical agitator rotating at between 300 and 350 rpm, a gas inlet tube (2 millimeters inside diameter) located just above the agitator blades for the addition of CO₂, a distillation column, and condenser under nitrogen gas.

EXAMPLE 1

ETHYLENE DIAMINE

[073] In Example 1, ethylene diamine was introduced concomitantly with the lime slurry to neutralize the alkyl hydroxy benzoic acid and reacted with CO₂.

[074] To a beaker was charged 175.8 grams of methanol, 222.5 grams of xylene solvent, and 175.8 grams of calcium hydroxide. The mixture was stirred for several minutes to obtain a lime slurry.

[075] To the glass reactor equipped with heating and cooling capability and fitted with a stainless steel mechanical agitator rotating at 350 rpm, a gas inlet tube (2 mm inside diameter) located just above the agitator blades for the addition of CO₂, a distillation column, and condenser was charged the lime slurry, and 76.1 g of ethylene diamine. The mixture was stirred for several minutes. Next, 1820.4 g of alkyl hydroxy benzoic acid (C14-16-18 alkyl hydroxy benzoic acid) was introduced. The resulting mixture was stirred for 15 min at 40°C. The reactor was cooled down to 30°C in 15 min. 56.9 g of CO₂ were introduced over 60 min at 0.95g/min. Then 55.5 g of CO₂ were introduced over 58 min at 0.95 g/min. During the reaction with CO₂ the reactor temperature increased from 30°C to 40°C.

[076] Then the first distillation step started under atmospheric pressure by heating the reactor from 40°C to 65°C in 15 min, then from 65°C to 93°C in 60 min, and then from 93°C to 128°C in 30 min. During this step methanol, water and some

of meta xylene were boiled off. At the end of this distillation step 613.4 g of 140N lube oil was charged to the reactor. Then the product was charged in a laboratory centrifuge running at 35000 G to separate insoluble solid products. The liquid part was charged in a 4 liters round bottom reactor, and xylene was distilled by heating the product to 170°C during approximately 45 min under 30 millimeters Hg vacuum and holding the product at 170°C under 30 millimeters Hg vacuum for 60 minutes. Vacuum was broken down with air and cooled down to ambient.

EXAMPLE 2

DIPHENYL AMINE

[077] In Example 2, diphenyl amine was introduced concomitantly with the lime slurry to neutralize the alkyl hydroxy benzoic acid and reacted with CO₂.

[078] To a beaker was charged 150 grams of methanol, 222.5 grams of xylene solvent, and 150 grams of calcium hydroxide. The mixture was stirred for several minutes to obtain a lime slurry.

[079] To the glass reactor equipped with heating and cooling capability and fitted with a stainless steel mechanical agitator rotating at 350 rpm, a gas inlet tube (2 mm inside diameter) located just above the agitator blades for the addition of CO₂, a distillation column, and condenser was charged the lime slurry, and 200 g of diphenyl amine. The mixture was stirred for several minutes. Then, 1820.4 grams of alkyl hydroxy benzoic acid (C14-16-18 alkyl hydroxy benzoic acid) was introduced. The mixture was stirred for 15 min at 40°C. The stirred mixture was cooled down to 30°C in 15 min. Next, 48.5 grams of CO₂ were introduced over 51 min at 0.95g/min – temperature increased from 30°C to 35°C. Then 52 grams of CO₂ were introduced over 55 min at 0.95g/min – temperature increased from 35°C to 40°C.

[080] Then the first distillation step started under atmospheric pressure by heating the reactor from 40°C to 65°C in 15 min, then from 65°C to 93°C in 60 min, then from 93°C to 128°C in 30 min. During this step methanol, water and some of meta xylene were boiled off. At the end of this distillation step 613.4 grams of 140N

lube oil was charged to the reactor. Then the product is charged in a laboratory centrifuge running at 35000 G to separate insoluble solid products.

[081] The liquid part was charged in a 4 liters round bottom reactor, and xylene was distilled by heating the product to 170°C and holding the product at 170°C during 60 min under 30 millimeters Hg vacuum. Vacuum was broken down with air and cooled down to ambient.

EXAMPLES 3

DIPHENYL AMINE

[082] In Example 3, diphenyl amine was introduced after neutralization of the alkyl hydroxy benzoic acid by lime and reacted with CO₂.

[083] To a beaker was charged 150 grams of methanol, 222.5 grams of xylene solvent, and 150 grams of calcium hydroxide. The mixture was stirred for several minutes to obtain a lime slurry.

[084] To the glass reactor equipped with heating and cooling capability and fitted with a stainless steel mechanical agitator rotating at 350 rpm, a gas inlet tube (2 mm inside diameter) located just above the agitator blades for the addition of CO₂, a distillation column, and condenser was charged the lime slurry. Then 1820.4 grams of alkyl hydroxy benzoic acid (C14-16-18 alkyl hydroxy benzoic acid) was introduced. The mixture was stirred for 15 min at 40°C. Then 200 grams of diphenyl amine was introduced in the glass reactor and the stirred mixture was cooled down to 30°C in 15 min. Next, 48.5 grams of CO₂ were introduced over 51 min at 0.95g/min – temperature increased from 30°C to 35°C. Then 52 grams of CO₂ were introduced over 55 min at 0.95g/min – temperature increased from 35°C to 40°C.

[085] Then the first distillation step started under atmospheric pressure by heating the reactor from 40°C to 65°C in 15 min, then from 65°C to 93°C in 60 min, then from 93°C to 128°C in 30 min. During this step methanol, water and some of meta xylene were boiled off. At the end of this distillation step 613.4 grams of 140N

lube oil was charged to the reactor. Then the product is charged in a laboratory centrifuge running at 35000 G to separate insoluble solid products.

[086] The liquid part was charged in a 4 liters round bottom reactor, and xylene was distilled by heating the product to 170°C and holding the product at 170°C during 60 min under 30 millimeters Hg vacuum. Vacuum was broken down with air and cooled down to ambient.

EXAMPLE 4

ETHANOL AMINE

[087] In Example 4, ethanol amine was introduced after neutralization of the alkyl hydroxy benzoic acid by lime and reacted with CO₂.

[088] To a beaker was charged 130 grams of methanol, 222.5 grams of xylene solvent, and 130 grams of calcium hydroxide. The mixture was stirred for several minutes to obtain a lime slurry.

[089] To the glass reactor equipped with heating and cooling capability and fitted with a stainless steel mechanical agitator rotating at 350 rpm, a gas inlet tube (2 mm inside diameter) located just above the agitator blades for the addition of CO₂, a distillation column, and condenser was charged the lime slurry. Then 1820.4 grams of alkyl hydroxy benzoic acid (C14-16-18 alkyl hydroxy benzoic acid) was introduced. The mixture was stirred for 15 min at 40°C. Then 70 grams of ethanolamine was introduced in the glass reactor and the stirred mixture was cooled down to 30°C in 15 min. Next, 25 grams of CO₂ were introduced over 26 min at 0.95g/min – temperature increased from 30°C to -34°C. Then 51.3 grams of CO₂ were introduced over 54 min at 0.95g/min – temperature increased from 34°C °C to 40°C.

[090] Then the first distillation step started under atmospheric pressure by heating the reactor from 40°C to 65°C in 15 min, then from 65°C to 93°C in 60 min, then from 93°C to 128°C in 30 min. During this step methanol, water and some of meta xylene were boiled off. At the end of this distillation step 613.4 grams of 140N lube oil was charged to the reactor. Then the product is charged in a laboratory centrifuge running at 35000 G to separate insoluble solid products.

[091] The liquid part was charged in a 4 liters round bottom reactor, and xylene was distilled by heating the product to 170°C and holding the product at 170°C during 60 min under 30 millimeters Hg vacuum. Vacuum was broken down with air and cooled down to ambient.

EXAMPLES 5

N-phenyl phenylene di-amine

[092] In Example 5, N-phenyl phenylene di-amine was introduced after neutralization of the alkyl hydroxy benzoic acid by lime and reacted with CO₂.

[093] To a beaker was charged 85 grams of methanol, 222.5 grams of xylene solvent, and 85 grams of calcium hydroxide. The mixture was stirred for several minutes to obtain a lime slurry.

[094] To the glass reactor equipped with heating and cooling capability and fitted with a stainless steel mechanical agitator rotating at 350 rpm, a gas inlet tube (2 mm inside diameter) located just above the agitator blades for the addition of CO₂, a distillation column, and condenser was charged the lime slurry. Then 1820.4 grams of alkyl hydroxy benzoic acid (C14-16-18 alkyl hydroxy benzoic acid) was introduced. The mixture was stirred for 15 min at 40°C. Then 200 grams of N phenyl phenylene diamine was introduced in the glass reactor and the stirred mixture was cooled down to 30°C in 15 min. Next, 16.4 grams of CO₂ were introduced over 17 min at 0.95g/min – temperature increased from 30°C to 32°C. Then 47.8 grams of CO₂ were introduced over 55 min at 0.95g/min – temperature increased from 32°C to 40°C.

[095] Then the first distillation step started under atmospheric pressure by heating the reactor from 40°C to 65°C in 15 min, then from 65°C to 93°C in 60 min, then from 93°C to 128°C in 30 min. During this step methanol, water and some of meta xylene were boiled off. At the end of this distillation step 613.4 grams of 140N lube oil was charged to the reactor. Then the product is charged in a laboratory centrifuge running at 35000 G to separate insoluble solid products.

[096] The liquid part was charged in a 4 liters round bottom reactor, and xylene was distilled by heating the product to 170°C and holding the product at 170°C during 60 min under 30 millimeters Hg vacuum. Vacuum was broken down with air and cooled down to ambient.

EXAMPLE 6

TRI-ETHYLENE TETRA-AMINE

[097] In Example 6, tri-ethylene tetra-amine was introduced after neutralization of the alkyl hydroxy benzoic acid by lime and reacted with CO₂.

[098] In a beaker were charged 65 grams of methanol, 115.7 grams of xylene solvent, and 65 grams of calcium hydroxide. The mixture was stirred for several minutes to obtain a lime slurry.

[099] To the glass reactor equipped with heating and cooling capability and fitted with a stainless steel mechanical agitator rotating at 350 rpm, a gas inlet tube (2 mm inside diameter) located just above the agitator blades for the addition of CO₂, a distillation column, and condenser was charged the lime slurry. Then 1820.4 grams of alkyl hydroxy benzoic acid (C14-16-18 alkyl hydroxy benzoic acid) was introduced. The mixture was stirred for 15 min at 40°C. Then 50 grams of tri-ethylene tetramine was introduced in the glass reactor and the stirred mixture was cooled down to 30°C in 20min . Then 15 grams of CO₂ were introduced over 16 min at 0.95g/min – temperature increased from 30°C to 35°C.

[0100] In a beaker were charged 60 grams of methanol, 106.8 grams of xylene solvent, 60 grams of calcium hydroxide, stirred during few minutes to obtain a lime slurry. The lime slurry was charged to the reactor. Then 24.1 grams of CO₂ were introduced over 25 min at 0.95g/min – temperature increased from 35°C to 40°C. Then the first distillation step started under atmospheric pressure by heating the reactor from 40°C to 65°C in 15 min, then from 65°C to 93°C in 60 min, then from 93°C to 128°C in 30 min. During this step methanol, water and some of meta xylene are boiled off. At the end of this distillation step 613.4 grams of 140N lube oil was charged to

the reactor. Then the product is charged in a laboratory centrifuge running at 35000 G to separate insoluble solid products. The liquid part was charged in a 4 liters round bottom reactor, and xylene was distilled by heating the product to 170°C and holding the product at 170°C during 60 min under 30 millimeters Hg vacuum. Vacuum was broken down with air and cooled down to ambient.

EXAMPLE 7

1,4-DIAZABICYCLO[2.2.2]OCTANE

[0101] In Example 7, 1,4-Diazabicyclo[2.2.2]octane was introduced after neutralization of the alkyl hydroxy benzoic acid by lime and reacted with CO₂.

[0102] In a beaker were charged 65 grams of methanol, 222.5 grams of xylene solvent, and 65 grams of calcium hydroxide. The mixture was stirred for several minutes to obtain a lime slurry.

[0103] To the glass reactor equipped with heating and cooling capability and fitted with a stainless steel mechanical agitator rotating at 350 rpm, a gas inlet tube (2 mm inside diameter) located just above the agitator blades for the addition of CO₂, a distillation column, and condenser was charged the lime slurry. Then 1820.4 grams of alkyl hydroxy benzoic acid (C14-16-18 alkyl hydroxy benzoic acid) was introduced. The mixture was stirred for 15 min, temperature 40°C. Then 190 grams of 1,4-Diazabicyclo[2.2.2]octane was introduced in the glass reactor and the stirred mixture was cooled down to 30°C in 15 min. Then 74.5 grams of CO₂ were introduced at 0.95g/min (79 minutes) – temperature increased from 30°C to 40°C. Then the first distillation step started under atmospheric pressure by heating the reactor from 40°C to 65°C in 15 min, then from 65°C to 93°C in 60 min, then from 93°C to 128°C in 30 min. During this step methanol, water and some of meta xylene are boiled off. At the end of this distillation step 613.4 grams of 140N lube oil was charged to the reactor. Then the product is charged in a laboratory centrifuge running at 35000 G to separate insoluble solid products. The liquid part was charged in a 4 liters round bottom reactor, and xylene was distilled by heating the product to 170°C and holding the

product at 170°C during 60 min under 30 millimeters Hg vacuum. Vacuum was broken down with air and cooled down to ambient.

EXAMPLE 8

1,4-DIAZABICYCLO[2.2.2]OCTANE

[0104] In Example 8, 1,4-Diazabicyclo[2.2.2]octane was introduced after neutralization of the alkyl hydroxy benzoic acid by lime and reacted with ethylene carbonate.

[0105] In a beaker were charged 65 grams of methanol, 222.5 grams of xylene solvent, and 65 grams of calcium hydroxide. The mixture was stirred for several minutes to obtain a lime slurry.

[0106] To the glass reactor equipped with heating and cooling capability and fitted with a stainless steel mechanical agitator rotating at 350 rpm, a gas inlet tube (2 mm inside diameter) located just above the agitator blades for the addition of CO₂, a distillation column, and condenser was charged the lime slurry. Then 1820.4 grams of alkyl hydroxy benzoic acid (C14-16-18 alkyl hydroxy benzoic acid) was introduced. The mixture was stirred for 15 min, temperature 40°C. Then 200 grams of 1,4-Diazabicyclo[2.2.2]octane was introduced in the glass reactor and the stirred mixture was heated to 45°C in 20 min. Then 314 grams of ethylene carbonate were introduced in 30 min— temperature increased to 45 - 50°C. Then the first distillation step started under atmospheric pressure by heating the reactor from 50°C °C to 65°C in 15 min, then from 65°C to 93°C in 60 min, then from 93°C to 128°C in 30 min. During this step methanol, water and some of meta xylene are boiled off. At the end of this distillation step 613.4 grams of 140N lube oil was charged to the reactor. Then the product is charged in a laboratory centrifuge running at 35000 G to separate insoluble solid products. The liquid part was charged in a 4 liters round bottom reactor, and xylene was distilled by heating the product to 170°C and holding the product at 170°C during 60 min under 30 millimeters Hg vacuum. Vacuum was broken down with air and cooled down to ambient.

EXAMPLE 9

1,4-DIAZABICYCLO[2.2.2]OCTANE

[0107] In Example 9, 1,4-Diazabicyclo[2.2.2]octane was introduced after neutralization of the alkyl hydroxy benzoic acid by lime.

[0108] To a beaker was charged 65 grams of methanol, 222.5 grams of xylene solvent, and 65 grams of calcium hydroxide. The mixture was stirred for several minutes to obtain a lime slurry.

[0109] To the glass reactor equipped with heating and cooling capability and fitted with a stainless steel mechanical agitator rotating at 350 rpm, a gas inlet tube (2 mm inside diameter) located just above the agitator blades for the addition of CO₂, a distillation column, and condenser was charged the lime slurry. Then 1820.4 grams of alkyl hydroxy benzoic acid (C14-16-18 alkyl phenol) was introduced. The mixture was stirred for 15 min, temperature 40°C. Then 190 grams of 1,4-Diazabicyclo[2.2.2]octane was introduced in the glass reactor and the stirred mixture was maintained at 40°C in 15 min. Then the first distillation step started under atmospheric pressure by heating the reactor from 40°C to 65°C in 15 min, then from 65°C to 93°C in 60 min, then from 93°C to 128°C in 30 min. During this step methanol, water and some of meta xylene are boiled off. At the end of this distillation step 613.4 grams of 140N lube oil was charged to the reactor. Then the product is charged in a laboratory centrifuge running at 35000 G to separate insoluble solid products. The liquid part was charged in a 4 liters round bottom reactor, and xylene was distilled by heating the product to 170°C and holding the product at 170°C during 60 min under 30 millimeters Hg vacuum. Vacuum was broken down with air and cooled down to ambient.

EXAMPLE 10

1,4-DIAZABICYCLO[2.2.2]OCTANE

[0110] In Example 10, 1,4-Diazabicyclo[2.2.2]octane was introduced after neutralization of the alkyl hydroxy benzoic acid by lime.

[0111] In a beaker were charged 65 grams of methanol, 222.5 grams of xylene solvent, and 65 grams of calcium hydroxide. The mixture was stirred for several minutes to obtain a lime slurry.

[0112] To the glass reactor equipped with heating and cooling capability and fitted with a stainless steel mechanical agitator rotating at 350 rpm, a gas inlet tube (2 mm inside diameter) located just above the agitator blades for the addition of CO₂, a distillation column, and condenser was charged the lime slurry. Then 2007.5 grams of alkyl hydroxy benzoic acid (C20-24 – 23% branched alkyl hydroxy benzoic acid) was introduced. The mixture was stirred for 15 min, temperature 40°C. Then 190 grams of 1,4-Diazabicyclo[2.2.2]octane was introduced in the glass reactor and the stirred mixture was maintained 30 min at 40°C. Then the first distillation step started under atmospheric pressure by heating the reactor from 40°C to 65°C in 15 min, then from 65°C to 93°C in 60 min, then from 93°C to 128°C in 30 min. During this step methanol, water and some of meta xylene are boiled off. At the end of this distillation step 613.4 grams of 140N lube oil was charged to the reactor. Then the product is charged in a laboratory centrifuge running at 35000 G to separate insoluble solid products. The liquid part was charged in a 4 liters round bottom reactor, and xylene was distilled by heating the product to 170°C and holding the product at 170°C during 60 min under 30 millimeters Hg vacuum. Vacuum was broken down with air and cooled down to ambient.

EXAMPLE 11

1,4-DIAZABICYCLO[2.2.2]OCTANE

[0113] In Example 11, 1,4-Diazabicyclo[2.2.2]octane was introduced after neutralization of the alkyl hydroxy benzoic acid by lime and reacted with CO₂.

[0114] In a beaker were charged 62 grams of methanol, 115.7 grams of xylene solvent, and 62 grams of calcium hydroxide. The mixture was stirred for several minutes to obtain a lime slurry.

[001] To the glass reactor equipped with heating and cooling capability and fitted with a stainless steel mechanical agitator rotating at 350 rpm, a gas inlet tube (2 mm inside diameter) located just above the agitator blades for the addition of CO₂, a distillation column and condenser was charged the lime slurry. Then 2007.5 grams of alkyl hydroxy benzoic acid (C20-24 – 23% branched alkyl hydroxy benzoic acid) was introduced. The mixture was stirred for 15 min, temperature 40°C. Then 170 grams of 1,4-Diazabicyclo[2.2.2]octane was introduced in the glass reactor and the stirred mixture was cooled to 30°C in 15 min. Then 66.7 grams of CO₂ were introduced over 70 min at 0.95g/min – temperature increased from 30°C to 37°C.

[0115] In a beaker were charged 38 grams of methanol, 106.8 grams of xylene solvent, 38 grams of calcium hydroxide, stirred during few minutes to obtain a lime slurry. The lime slurry was charged to the reactor. Then 12.2 grams of CO₂ were introduced over 13 min at 0.95g/min – temperature increased from 37°C to 40°C. Then the first distillation step started under atmospheric pressure by heating the reactor from 40°C to 65°C in 15 min, then from 65°C to 93°C in 60 min, then from 93°C to 128°C in 30 min. During this step methanol, water and some of meta xylene are boiled off. At the end of this distillation step 613.4 grams of 140N lube oil was charged to the reactor. Then the product is charged in a laboratory centrifuge running at 35000 G to separate insoluble solid products. The liquid part was charged in a 4 liters round bottom reactor, and xylene was distilled by heating the product to 170°C and holding the product at 170°C during 60 min under 30 millimeters Hg vacuum. Vacuum was broken down with air and cooled down to ambient.

EXAMPLE 12

TRI-ETHYLENE TETRA-AMINE

[0116] In Example 12, tri-ethylene tetra-amine was introduced after neutralization of the alkyl hydroxy benzoic acid by lime and reacted with ethylene carbonate.

[0117] In a beaker were charged 65 grams of methanol, 222.5 grams of xylene solvent, and 65 grams of calcium hydroxide. The mixture was stirred for several minutes to obtain a lime slurry.

[0118] To the glass reactor equipped with heating and cooling capability and fitted with a stainless steel mechanical agitator rotating at 350 rpm, a gas inlet tube (2 mm inside diameter) located just above the agitator blades for the addition of CO₂, a distillation column, and condenser was charged the lime slurry. Then 1820.4 grams of alkyl hydroxy benzoic acid (C14-16-18 alkyl hydroxy acid) was introduced. The mixture was stirred for 15 min, temperature 40°C. Then 110 grams of tri-ethylene tetra-amine was introduced in the glass reactor and the stirred mixture was heated to 45°C in 20min. Then 132.5 grams of ethylene carbonate were introduced and the mixture was stirred during 30 min and heated to 50°C. Then the first distillation step started under atmospheric pressure by heating the reactor from 50°C to 65°C in 15 min, then from 65°C to 93°C in 60 min, then from 93°C to 128°C in 30 min. During this step methanol, water and some of meta xylene are boiled off. At the end of this distillation step 613.4 grams of 140N lube oil was charged to the reactor. Then the product is charged in a laboratory centrifuge running at 35000 G to separate insoluble solid products. The liquid part was charged in a 4 liters round bottom reactor, and xylene was distilled by heating the product to 170°C and holding the product at 170°C during 60 min under 30 millimeters Hg vacuum. Vacuum was broken down with air and cooled down to ambient.

EXAMPLE 13

C9 ALKYLATED DI-PHENYL AMINE

[0119] In Example 13, C9 alkylated di-phenyl amine was introduced after neutralization of the alkyl hydroxy benzoic acid by lime and reacted with CO₂.

[0120] In a beaker were charged 65 grams of methanol, 115.7 grams of xylene solvent, and 65 grams of calcium hydroxide. The mixture was stirred for several minutes to obtain a lime slurry.

[0121] To the glass reactor equipped with heating and cooling capability and fitted with a stainless steel mechanical agitator rotating at 350 rpm, a gas inlet tube (2 mm inside diameter) located just above the agitator blades for the addition of CO₂, a distillation column, and condenser was charged the lime slurry. Then 1820.4 grams of alkyl hydroxy benzoic acid (C14-16-18 alkyl hydroxy benzoic acid) was introduced. The mixture was stirred for 15 min, temperature 40°C. Then 570 grams of C9 alkylated di-phenyl amine was introduced in the glass reactor and the stirred mixture was cooled down to 30°C in 20 min. Then 67.5 grams of CO₂ were introduced over 71 min at 0.95g/min – temperature increased from 30°C to 36°C. In a beaker were charged 110.8 grams of methanol, 106.8 grams of xylene solvent, 110.8 grams of calcium hydroxide, stirred during few minutes to obtain a lime slurry. The lime slurry was charged to the reactor. Then 56.4 grams of CO₂ were introduced over 59 min at 0.95g/min – temperature increased from 36°C to 40°C. Then the first distillation step started under atmospheric pressure by heating the reactor from 40°C to 65°C in 15 min, then from 65°C to 93°C in 60 min, then from 93°C to 128°C in 30 min. During this step methanol, water and some of meta xylene are boiled off. At the end of this distillation step 600 grams of 140N lube oil was charged to the reactor. Then the product is charged in a laboratory centrifuge running at 35000 G to separate insoluble solid products. The liquid part was charged in a 4 liters round bottom reactor, and xylene was distilled by heating the product to 170°C and holding the product at 170°C during 60 min under 30 millimeters Hg vacuum. Vacuum was broken down with air and cooled down to ambient.

EXAMPLE 14

C9 ALKYLATED DI-PHENYL AMINE

[0122] In Example 14, C9 alkylated di-phenyl amine was introduced after neutralization of the alkyl hydroxy benzoic acid by lime and reacted with CO₂.

[0123] In a beaker were charged 62 grams of methanol, 115.7 grams of xylene solvent, and 62 grams of calcium hydroxide. The mixture was stirred for several minutes to obtain a lime slurry.

[0124] To the glass reactor equipped with heating and cooling capability and fitted with a stainless steel mechanical agitator rotating at 350 rpm, a gas inlet tube (2 mm inside diameter) located just above the agitator blades for the addition of CO₂, a distillation column, and condenser was charged the lime slurry. Then 2007.5 grams of alkyl hydroxy benzoic acid (C20 – 24 – branched to 23%) was introduced. The mixture was stirred for 15 min, temperature 40°C. Then 570 grams of C9 alkylated di-phenyl amine was introduced in the glass reactor and the stirred mixture was cooled down to 30°C in 20 min. Then 67.5 grams of CO₂ were introduced over 71 min at 0.95g/min – temperature increased from 30°C to 36°C. In a beaker were charged 113.8 grams of methanol, 106.8 grams of xylene solvent, 113.8 grams of calcium hydroxide, stirred during few minutes to obtain a lime slurry. The lime slurry was charged to the reactor. Then 56.4 grams of CO₂ were introduced over 59 min at 0.95g/min – temperature increased from 36°C to 40°C. Then the first distillation step started under atmospheric pressure by heating the reactor from 40°C to 65°C in 15 min, then from 65°C to 93°C in 60 min, then from 93°C to 128°C in 30 min. During this step methanol, water and some of meta xylene are boiled off. At the end of this distillation step 500 grams of 140N lube oil was charged to the reactor. Then the product is charged in a laboratory centrifuge running at 35000 G to separate insoluble solid products. The liquid part was charged in a 4 liters round bottom reactor, and xylene was distilled by heating the product to 170°C and holding the product at 170°C during 60 min under 30 millimeters Hg vacuum. Vacuum was broken down with air and cooled down to ambient.

EXAMPLE 15

C9 ALKYLATED DI-PHENYL AMINE

[0125] In Example 15, C9 alkylated di-phenyl amine was introduced after neutralization of the alkyl hydroxy benzoic acid by lime.

[0126] In a beaker were charged 62 grams of methanol, 115.7 grams of xylene solvent, and 62 grams of calcium hydroxide. The mixture was stirred for several minutes to obtain a lime slurry.

[0127] To the glass reactor equipped with heating and cooling capability and fitted with a stainless steel mechanical agitator rotating at 350 rpm, a gas inlet tube (2 mm inside diameter) located just above the agitator blades for the addition of CO₂, a distillation column, and condenser was charged the lime slurry. Then 2007.5 grams of alkyl hydroxy benzoic acid (C20 – 24 – branched to 23%) was introduced. The mixture was stirred for 15 min, temperature 40°C. Then 1100 grams of C9 alkylated di-phenyl amine was introduced in the glass reactor and the stirred mixture was cooled down to 30°C in 15 min. In a beaker were charged 113.8 grams of methanol, 106.8 grams of xylene solvent, 113.8 grams of calcium hydroxide, stirred during few minutes to obtain a lime slurry. The lime slurry was charged to the reactor. Then 56.4 grams of CO₂ were introduced over 59 min at 0.95g/min – temperature increased from 30°C to 40°C. Then the first distillation step started under atmospheric pressure by heating the reactor from 40°C to 65°C in 15 min, then from 65°C to 93°C in 60 min, then from 93°C to 128°C in 30 min. During this step methanol, water and some of meta xylene are boiled off. At the end of this distillation step 500 grams of 140N lube oil was charged to the reactor. Then the product is charged in a laboratory centrifuge running at 35000 G to separate insoluble solid products. The liquid part was charged in a 4 liters round bottom reactor, and xylene was distilled by heating the product to 170°C and holding the product at 170°C during 60 min under 30 millimeters Hg vacuum. Vacuum was broken down with air and cooled down to ambient.

EXAMPLE 16

BENZYL AMINE

[0128] In Example 16, benzyl amine was introduced after neutralization of the alkyl hydroxy benzoic acid by lime and reacted with CO₂.

[0129] In a beaker were charged 65 grams of methanol, 222.5 grams of xylene solvent, and 65 grams of calcium hydroxide. The mixture was stirred for several minutes to obtain a lime slurry.

[0130] To the glass reactor equipped with heating and cooling capability and fitted with a stainless steel mechanical agitator rotating at 350 rpm, a gas inlet tube (2 mm inside diameter) located just above the agitator blades for the addition of CO₂, a distillation column, and condenser was charged the lime slurry. Then 1820.4 grams of alkyl hydroxy benzoic acid (C14-16-18 alkyl hydroxy benzoic acid) was introduced. The mixture was stirred for 15 min, temperature 40°C. Then 400 grams of benzyl amine was introduced in the glass reactor and the stirred mixture was cooled down to 30°C in 20 min. Then 164.3 grams of CO₂ were introduced over 173 min at 0.95g/min – temperature increased from 30°C to 40°C. Then the first distillation step started under atmospheric pressure by heating the reactor from 40°C to 65°C in 15 min, then from 65°C to 93°C in 60 min, then from 93°C to 128°C in 30 min. During this step methanol, water and some of meta xylene are boiled off. At the end of this distillation step 613.4 grams of 140N lube oil was charged to the reactor. Then the product is charged in a laboratory centrifuge running at 35000 G to separate insoluble solid products. The liquid part was charged in a 4 liters round bottom reactor, and xylene was distilled by heating the product to 170°C and holding the product at 170°C during 60 min under 30 millimeters Hg vacuum. Vacuum was broken down with air and cooled down to ambient.

EXAMPLE 17

UREA

[0131] In Example 17, urea was introduced after neutralization of the alkyl hydroxy benzoic acid by lime and reacted with CO₂.

[0132] In a beaker were charged 65 grams of methanol, 222.5 grams of xylene solvent, and 65 grams of calcium hydroxide. The mixture was stirred for several minutes to obtain a lime slurry.

[0133] To the glass reactor equipped with heating and cooling capability and fitted with a stainless steel mechanical agitator rotating at 350 rpm, a gas inlet tube (2 mm inside diameter) located just above the agitator blades for the addition of CO₂, a distillation column, and condenser was charged the lime slurry. Then 1820.4 grams of alkyl hydroxy benzoic acid (C14-16-18 alkyl hydroxy benzoic acid) was introduced. The mixture was stirred for 15 min, temperature 40°C. Then 85 grams of urea was introduced in the glass reactor and the stirred mixture was cooled down to 30°C in 15 min. Then 62.3 grams of CO₂ were introduced over 67 min at 0.95g/min – temperature increased from 30°C to 40°C. Then the first distillation step started under atmospheric pressure by heating the reactor from 40°C to 65°C in 15 min, then from 65°C to 93°C in 60 min, then from 93°C to 128°C in 30 min. During this step methanol, water and some of meta xylene are boiled off. At the end of this distillation step 613.4 grams of 140N lube oil was charged to the reactor. Then the product is charged in a laboratory centrifuge running at 35000 G to separate insoluble solid products. The liquid part was charged in a 4 liters round bottom reactor, and xylene was distilled by heating the product to 170°C and holding the product at 170°C during 60 min under 30 millimeters Hg vacuum. Vacuum was broken down with air and cooled down to ambient.

EXAMPLE 18

DIMEYHYL PIPERAZINE

[0134] In Example 18, dimethyl piperazine was introduced after neutralization of the alkyl hydroxy benzoic acid by lime and reacted with CO₂.

[0135] In a beaker were charged 100 grams of methanol, 222.5 grams of xylene solvent, and 100 grams of calcium hydroxide. The mixture was stirred for several minutes to obtain a lime slurry.

[0136] To the glass reactor equipped with heating and cooling capability and fitted with a stainless steel mechanical agitator rotating at 350 rpm, a gas inlet tube (2 mm inside diameter) located just above the agitator blades for the addition of CO₂, a distillation column, and condenser was charged the lime slurry. Then 2007.5 grams of

alkyl hydroxy benzoic acid (C20-24 – 23% isomerized alkyl hydroxy benzoic acid) was introduced. The mixture was stirred for 15 min, temperature 40°C. Then 150 grams of dimethyl piperazine was introduced in the glass reactor and the stirred mixture was maintained for 15 min at 40°C and cooled down to 30°C in 20 min. Then 11.6 grams of CO₂ were introduced in 13 min at 0.95g/min – temperature increased from 30°C to 36°C. Then 57.8 grams of CO₂ were introduced in 61 min at 0.95g/min – temperature increased from 36°C to 60°C. Then the first distillation step started under atmospheric pressure by heating the reactor from 60°C to 65°C in 15 min, then from 65°C to 93°C in 60 min, then from 93°C to 128°C in 30 min. During this step methanol, water and some of meta xylene are boiled off. At the end of this distillation step 613.4 grams of 140N lube oil was charged to the reactor. Then the product is charged in a laboratory centrifuge running at 35000 G to separate insoluble solid products. The liquid part was charged in a 4 liters round bottom reactor, and xylene was distilled by heating the product to 170°C and holding the product at 170°C during 60 min under 30 millimeters Hg vacuum. Vacuum was broken down with air and cooled down to ambient.

EXAMPLE 19

DIMETHYL PIPERAZINE

[0137] In Example 19, dimethyl piperazine was introduced after neutralization of the alkyl hydroxy benzoic acid by lime.

[0138] In a beaker were charged 62 grams of methanol, 222.5 grams of xylene solvent, and 62 grams of calcium hydroxide. The mixture was stirred for several minutes to obtain a lime slurry.

[0139] To the glass reactor equipped with heating and cooling capability and fitted with a stainless steel mechanical agitator rotating at 350 rpm, a gas inlet tube (2 mm inside diameter) located just above the agitator blades for the addition of CO₂, a distillation column, and condenser was charged the lime slurry. Then 2007.5 grams of alkyl hydroxy benzoic acid (C20-24 – 23% isomerized alkyl hydroxy benzoic acid) was introduced. The mixture was stirred for 15 min, temperature 40°C. Then 150 grams of

dimethyl piperazine was introduced in the glass reactor and the stirred mixture was maintained for 15 min at 40°C and heated to 50°C in 30 min. Then the first distillation step started under atmospheric pressure by heating the reactor from 50°C to 65°C in 15 min, then from 65°C to 93°C in 60 min, then from 93°C to 128°C in 30 min. During this step methanol, water and some of meta xylene are boiled off. At the end of this distillation step 425 grams of 140N lube oil was charged to the reactor. Then the product is charged in a laboratory centrifuge running at 35000 G to separate insoluble solid products. The liquid part was charged in a 4 liters round bottom reactor, and xylene was distilled by heating the product to 170°C and holding the product at 170°C during 60 min under 30 millimeters Hg vacuum. Vacuum was broken down with air and cooled down to ambient.

EXAMPLE 20

N-ETHYL BUTYL AMINE

[0140] In Example 20, N-ethyl butyl amine was introduced after neutralization of the alkyl hydroxy benzoic acid by lime and reacted with CO₂.

[0141] In a beaker were charged 100 grams of methanol, 222.5 grams of xylene solvent, and 100 grams of calcium hydroxide. The mixture was stirred for several minutes to obtain a lime slurry.

[0142] To the glass reactor equipped with heating and cooling capability and fitted with a stainless steel mechanical agitator rotating at 350 rpm, a gas inlet tube (2 mm inside diameter) located just above the agitator blades for the addition of CO₂, a distillation column, and condenser was charged the lime slurry. Then 2007.5 grams of alkyl hydroxy benzoic acid (C20-24 – 23% isomerized alkyl hydroxy benzoic acid) was introduced. The mixture was stirred for 15 min, temperature 40°C. Then 200 grams of N-ethyl butyl amine was introduced in the glass reactor and cooled down to 30°C in 20 min. Then 11.6 grams of CO₂ were introduced in 12 min at 0.95g/min – temperature increased from 30°C to 34°C. Then 87 grams of CO₂ were introduced in 92 min at 0.95g/min - temperature increased from 34°C to 60°C. Then the first distillation step

started under atmospheric pressure by heating the reactor from 60°C to 65°C in 15 min, then from 65°C to 93°C in 60 min, then from 93°C to 128°C in 30 min. During this step methanol, water and some of meta xylene are boiled off. At the end of this distillation step 613.4 grams of 140N lube oil was charged to the reactor. Then the product is charged in a laboratory centrifuge running at 35000 G to separate insoluble solid products. The liquid part was charged in a 4 liters round bottom reactor, and xylene was distilled by heating the product to 170°C and holding the product at 170°C during 60 min under 30 millimeters Hg vacuum. Vacuum was broken down with air and cooled down to ambient.

EXAMPLE 21

N-ETHYL BUTYL AMINE

[0143] In Example 21, N-ethyl butyl amine was introduced after neutralization of the alkyl hydroxy benzoic acid by lime and reacted with ethylene carbonate.

[0144] In a beaker were charged 100 grams of methanol, 222.5 grams of xylene solvent, and 100 grams of calcium hydroxide. The mixture was stirred for several minutes to obtain a lime slurry.

[0145] To the glass reactor equipped with heating and cooling capability and fitted with a stainless steel mechanical agitator rotating at 350 rpm, a gas inlet tube (2 mm inside diameter) located just above the agitator blades for the addition of CO₂, a distillation column, and condenser was charged the lime slurry. Then 2007.5 grams of alkyl hydroxy benzoic acid (C20-24 – 23% isomerized alkyl hydroxy benzoic acid) was introduced. The mixture was stirred for 15 min, temperature 40°C. Then 200 grams of N-ethyl butyl amine was introduced in the glass reactor and the mixture was maintained at 40°C during 15 min. Then 433.9 grams of ethylene carbonate were introduced in 30 min – temperature increased from 40°C to 50°C. Then the mixture was maintained at 50°C during 15 min. Then the first distillation step started under atmospheric pressure by heating the reactor from 50°C to 65°C in 15 min, then from 65°C to 93°C in 60 min, then from 93°C to 128°C in 30 min. During this step methanol,

water and some of meta xylene are boiled off. At the end of this distillation step 613.4 grams of 140N lube oil was charged to the reactor. Then the product is charged in a laboratory centrifuge running at 35000 G to separate insoluble solid products. The liquid part was charged in a 4 liters round bottom reactor, and xylene was distilled by heating the product to 170°C and holding the product at 170°C during 60 min under 30 millimeters Hg vacuum. Vacuum was broken down with air and cooled down to ambient.

EXAMPLE 22

N-ETHYL BUTYL AMINE

[0146] In Example 22, N-ethyl butyl amine was introduced after neutralization of the alkyl hydroxy benzoic acid by lime.

[0147] In a beaker were charged 65 grams of methanol, 222.5 grams of xylene solvent, and 65 grams of calcium hydroxide. The mixture was stirred for several minutes to obtain a lime slurry.

[0148] To the glass reactor equipped with heating and cooling capability and fitted with a stainless steel mechanical agitator rotating at 350 rpm, a gas inlet tube (2 mm inside diameter) located just above the agitator blades for the addition of CO₂, a distillation column, and condenser was charged the lime slurry. Then 2007.5 grams of alkyl hydroxy benzoic acid (C20-24 – 23% isomerized alkyl hydroxy benzoic acid) was introduced. The mixture was stirred for 15 min, temperature 40°C. Then 290 grams of N-ethyl butyl amine was introduced in the glass reactor and the mixture was maintained at 40°C during 15 min. Temperature was increased from 40°C to 50°C in 30 min. Then the first distillation step started under atmospheric pressure by heating the reactor from 50°C to 65°C in 15 min, then from 65°C to 93°C in 60 min, then from 93°C to 128°C in 30 min. During this step methanol, water and some of meta xylene are boiled off. At the end of this distillation step 613.4 grams of 140N lube oil was charged to the reactor. Then the product is charged in a laboratory centrifuge running at 35000 G to separate insoluble solid products. The liquid part was charged in a 4

liters round bottom reactor, and xylene was distilled by heating the product to 170°C and holding the product at 170°C during 60 min under 30 millimeters Hg vacuum. Vacuum was broken down with air and cooled down to ambient.

EXAMPLE 23

ISO-PROPYL METHYL AMINE

[0149] In Example 23, iso-propyl methyl amine was introduced after neutralization of the alkyl hydroxy benzoic acid by lime.

[0150] In a beaker were charged 62 grams of methanol, 222.5 grams of xylene solvent, and 62 grams of calcium hydroxide. The mixture was stirred for several minutes to obtain a lime slurry.

[0151] To the glass reactor equipped with heating and cooling capability and fitted with a stainless steel mechanical agitator rotating at 350 rpm, a gas inlet tube (2 mm inside diameter) located just above the agitator blades for the addition of CO₂, a distillation column, and condenser was charged the lime slurry. Then 2007.5 grams of alkyl hydroxy benzoic acid (C20-24 – 23% isomerized alkyl hydroxy benzoic acid) was introduced. The mixture was stirred for 15 min, temperature 40°C. Then 250 grams of Iso-propyl methyl amine was introduced in the glass reactor and the mixture was maintained at 40°C during 15 min. Temperature was increased from 40°C to 50°C in 30 min. Then the first distillation step started under atmospheric pressure by heating the reactor from 50°C to 65°C in 15 min, then from 65°C to 93°C in 60 min, then from 93°C to 128°C in 30 min. During this step methanol, water and some of meta xylene are boiled off. At the end of this distillation step 613.4 grams of 140N lube oil was charged to the reactor. Then the product is charged in a laboratory centrifuge running at 35000 G to separate insoluble solid products. The liquid part was charged in a 4 liters round bottom reactor, and xylene was distilled by heating the product to 170°C and holding the product at 170°C during 60 min under 30 millimeters Hg vacuum. Vacuum was broken down with air and cooled down to ambient.

EXAMPLE 24

C9 ALKYLATED DI-PHENYL AMINE

[0152] In Example 24, C9 alkylated di-phenyl amine was introduced after neutralization of alkyl or alkenyl aromatic sulfonic acid with lime and reacted with CO₂.

[0153] In a beaker were charged 21 grams of methanol, 147.5 grams of xylene solvent, and 21 grams of calcium hydroxide. The mixture was stirred for several minutes to obtain a lime slurry.

[0154] To the glass reactor equipped with heating and cooling capability and fitted with a stainless steel mechanical agitator rotating at 350 rpm, a gas inlet tube (2 mm inside diameter) located just above the agitator blades for the addition of CO₂, a distillation column, and condenser was charged the lime slurry. Then 313.4 grams of alkyl or alkenyl aromatic sulfonic acid (C20-24 alkyl or alkenyl aromatic sulfonic acid) was introduced during 15 min until 30°C. Then the mixture was maintained at 30°C for 15 min. Then 570 grams of C9 alkylated di-phenyl amine was introduced in the glass reactor and the stirred mixture was maintained for 40 min at 30°C. Then 67.5 grams of CO₂ were introduced in 68 min at 1.0 g/min – temperature increased from 30°C to 36°C. In a beaker were charged 90 grams of methanol, 200 grams of xylene solvent, and 90 grams of calcium hydroxide. The mixture was stirred for several minutes to obtain a lime slurry. To the glass reactor was charged the lime slurry previously made in the beaker. Then 48.8 grams of CO₂ were introduced in 49 min at 1.0 g/min - temperature increased from 36°C to 40°C. Then the first distillation step started under atmospheric pressure by heating the reactor from 40°C to 65°C in 15 min, then from 65°C to 93°C in 60 min, then from 93°C to 128°C in 30 min. During this step methanol, water and some of meta xylene are boiled off. At the end of this distillation step 400 grams of 600N lube oil was charged to the reactor. Then the product is charged in a laboratory centrifuge running at 35000 G to separate insoluble solid products. The liquid part was charged in a 4 liters round bottom reactor, and xylene was distilled by heating the product to 204°C and holding the product at 204°C during 10 min under

30 millimeters Hg vacuum. Vacuum was broken down with air and cooled down to ambient.

EXAMPLE 25

C9 ALKYLATED DI-PHENYL AMINE

[0155] In Example 25, C9 alkylated di-phenyl amine was introduced after neutralization of alkyl or alkenyl aromatic sulfonic acid with lime.

[0156] In a beaker were charged 211 grams of methanol, 347.5 grams of xylene solvent, and 211 grams of calcium hydroxide. The mixture was stirred for several minutes to obtain a lime slurry.

[0157] To the glass reactor equipped with heating and cooling capability and fitted with a stainless steel mechanical agitator rotating at 350 rpm, a gas inlet tube (2 mm inside diameter) located just above the agitator blades for the addition of CO₂, a distillation column, and condenser was charged the lime slurry. Then 311.2 grams of alkyl or alkenyl aromatic sulfonic acid (C20-24 alkyl or alkenyl aromatic sulfonic acid) was introduced during 15 min until 30°C. Then the mixture was maintained at 30°C for 15 min. Then 800 grams of C9 alkylated di-phenyl amine was introduced in the glass reactor and the stirred mixture was maintained for 40 min at 30°C. Then 92.8 grams of CO₂ were introduced in 93 min at 1.0 g/min – temperature increased from 30°C to 40°C.

[0158] Then the first distillation step started under atmospheric pressure by heating the reactor from 40°C to 65°C in 15 min, then from 65°C to 93°C in 60 min, then from 93°C to 128°C in 30 min. During this step methanol, water and some of meta xylene are boiled off. At the end of this distillation step 390 grams of 600N lube oil was charged to the reactor. Then the product is charged in a laboratory centrifuge running at 35000 G to separate insoluble solid products. The liquid part was charged in a 4 liters round bottom reactor, and xylene was distilled by heating the product to 204°C and holding the product at 204°C during 10 min under 30 millimeters Hg vacuum. Vacuum was broken down with air and cooled down to ambient.

EXAMPLE 26

1,4-DIAZABICYCLO[2.2.2]OCTANE

[0159] In Example 26, 1,4-Diazabicyclo[2.2.2]octane was introduced after neutralization of alkyl or alkenyl aromatic sulfonic acid with lime.

[0160] In a beaker were charged 21 grams of methanol, 247.5 grams of xylene solvent, and 21 grams of calcium hydroxide. The mixture was stirred for several minutes to obtain a lime slurry.

[0161] To the glass reactor equipped with heating and cooling capability and fitted with a stainless steel mechanical agitator rotating at 350 rpm, a gas inlet tube (2 mm inside diameter) located just above the agitator blades for the addition of CO₂, a distillation column, and condenser was charged the lime slurry. Then 305.8 grams of alkyl or alkenyl aromatic sulfonic acid (C₂₀₋₂₄ alkyl or alkenyl aromatic sulfonic acid) was introduced during 15 min until 30°C. Then the mixture temperature was increased from 30°C to 40°C in 20 min. Then 160 grams of 1,4-Diazabicyclo[2.2.2]octane was introduced in the glass reactor and the stirred mixture was maintained for 20 min at 40°C.

[0162] Then the first distillation step started under atmospheric pressure by heating the reactor from 40°C to 65°C in 15 min, then from 65°C to 93°C in 60 min, then from 93°C to 128°C in 30 min. During this step methanol, water and some of meta xylene are boiled off. At the end of this distillation step 400 grams of 600N lube oil was charged to the reactor. Then the product is charged in a laboratory centrifuge running at 35000 G to separate insoluble solid products. The liquid part was charged in a 4 liters round bottom reactor, and xylene was distilled by heating the product to 204°C and holding the product at 204°C during 10 min under 30 millimeters Hg vacuum. Vacuum was broken down with air and cooled down to ambient.

EXAMPLE 27

ALYLATED DIPHENYL AMINE

[0163] In Example 27, C9 alkylated di-phenyl amine was introduced after the formation of calcium carbonate and after the neutralization of alkyl or alkenyl aromatic sulfonic acid with lime.

[0164] In a beaker were charged 211 grams of methanol, 347.5 grams of xylene solvent, and 211 grams of calcium hydroxide. The mixture was stirred for several minutes to obtain a lime slurry.

[0165] To the glass reactor equipped with heating and cooling capability and fitted with a stainless steel mechanical agitator rotating at 350 rpm, a gas inlet tube (2 mm inside diameter) located just above the agitator blades for the addition of CO₂, a distillation column, and condenser was charged the lime slurry. Then 311.2 grams of alkyl or alkenyl aromatic sulfonic acid (C20-24 alkyl or alkenyl aromatic sulfonic acid) was introduced during 15 min until 32°C. Then the mixture was cooled to 25°C. Then 92.8 grams of CO₂ were introduced in 93 min at 1.0 g/min – temperature increased from 25°C to 32°C.

[0166] Then 800 grams of C9 alkylated di-phenyl amine was introduced 15 min in the glass reactor and reactor was cooled down to 30°C.

[0167] Then 94.7 grams of CO₂ were introduced in 95 min at 1.0 g/min – temperature increased from 30°C to 41°C.

[0168] Then the first distillation step started under atmospheric pressure by heating the reactor from 41°C to 65°C in 15 min, then from 65°C to 93°C in 60 min, then from 93°C to 128°C in 30 min. During this step methanol, water and some of meta xylene are boiled off. At the end of this distillation step 390 grams of 600N lube oil was charged to the reactor. Then the product is charged in a laboratory centrifuge running at 35000 G to separate insoluble solid products. The liquid part was charged in a 4 liters round bottom reactor, and xylene was distilled by heating the product to 204°C and holding the product at 204°C during 10 min under 30 millimeters Hg vacuum. Vacuum was broken down with air and cooled down to ambient.

EXAMPLE 28

2-PHENOXY ETHYL AMINE

[0169] In Example 28, 2-phenoxy ethyl amine was introduced after neutralization of the alkyl hydroxy benzoic acid by lime.

[0170] In a beaker were charged 12.7 grams of methanol, 54.7 grams of xylene, and 19.3 grams of calcium hydroxide. The mixture was stirred for several minutes to obtain a lime slurry.

[0171] To a 1L glass reactor equipped with heating capability and fitted with a stainless-steel mechanical agitator rotating at 350 rpm, a gas sparging tube located just above the agitator blades for the addition of CO₂, a Claisen adaptor and condenser, was charged the lime slurry. Then 200 grams of alkyl hydroxy benzoic acid (C20-24 – 23% isomerized alkyl hydroxy benzoic acid) was introduced dropwise over 15 minutes. The mixture was stirred for 15 min, temperature 40°C. Then 23.9 grams of 2-phenoxy ethyl amine was introduced in the glass reactor and the mixture was maintained at 40°C during 15 min. During this hold time, a mixture of 30.7 grams of methanol, 121.3 grams of xylene and 46.4 grams of calcium hydroxide were stirring in a beaker to obtain a second lime slurry. Over the next 156 minutes, this slurry was dripped into the glass reactor via peristaltic pump, as 29.2 grams of CO₂ was fed into the reaction through the glass sparger as follows: 1.7 grams over 11 minutes at 40°C, 14.5 grams over 76 minutes at 40°C to 53°C, and finally, 13.0 grams over 69 minutes over 53°C to 58°C.

[0172] Then the first distillation step started under atmospheric pressure by heating the reactor from 58°C to 65°C in 15 min, then from 65°C to 93°C in 60 min, then from 93°C to 128°C in 30 min. During this step methanol, water and some of meta xylene were boiled off. At the end of this distillation step 69.2 grams of 100R lube oil was charged to the reactor. Then the product was charged in a laboratory centrifuge running at 10000 RPM to separate insoluble solid products. The liquid part was charged back into the 1L reactor, and xylene was distilled by heating the product to 170°C and holding the product at 170°C during 60 min under 30 millimeters Hg vacuum. Vacuum was broken down with air and cooled down to ambient.

EXAMPLE 29

C20-24 ALKYLATED 2-PHENOXY ETHYL AMINE

[0173] In Example 29, C20-24 alkylated phenoxy ethyl amine was introduced after neutralization of the alkyl hydroxy benzoic acid by lime.

[0174] In a beaker were charged 12.7 grams of methanol, 54.7 grams of xylene, and 19.3 grams of calcium hydroxide. The mixture was stirred for several minutes to obtain a lime slurry.

[0175] To a 1L glass reactor equipped with heating capability and fitted with a stainless-steel mechanical agitator rotating at 350 rpm, a gas sparging tube located just above the agitator blades for the addition of CO₂, a Claisen adaptor and condenser, was charged the lime slurry. Then 200 grams of alkyl hydroxy benzoic acid (C20-24 – 23% isomerized alkyl hydroxy benzoic acid) was introduced dropwise over 15 minutes. The mixture was stirred for 15 min, temperature 40°C. Then 74.9 grams of C20-24 alkylated 2-phenoxy ethyl amine was introduced in the glass reactor and the mixture was maintained at 40°C during 15 min. During this hold time, a mixture of 30.7 grams of methanol, 121.3 grams of xylene and 46.4 grams of calcium hydroxide were stirring in a beaker to obtain a second lime slurry. Over the next 156 minutes, this slurry was dripped into the glass reactor via peristaltic pump, as 29.2 grams of CO₂ was fed into the reaction through the glass sparger as follows: 1.7 grams over 11 minutes at 40°C, 14.5 grams over 76 minutes at 40°C to 53°C, and finally, 13.0 grams over 69 minutes over 53°C to 58°C.

[0176] Then the first distillation step started under atmospheric pressure by heating the reactor from 58°C to 65°C in 15 min, then from 65°C to 93°C in 60 min, then from 93°C to 128°C in 30 min. During this step methanol, water and some of meta xylene were boiled off. At the end of this distillation step 69.2 grams of 100R lube oil was charged to the reactor. Then the product was charged in a laboratory centrifuge running at 10000 RPM to separate insoluble solid products. The liquid part was charged back into the 1L reactor, and xylene was distilled by heating the product to

170°C and holding the product at 170°C during 60 min under 30 millimeters Hg vacuum. Vacuum was broken down with air and cooled down to ambient.

EXAMPLE 30

C9 ALKYLATED DI-PHENYL AMINE AND GLYCINE

[0177] In Example 30, the alkyl hydroxy benzoic acid was neutralized with lime. Then after neutralization of the benzoic acid, 16 grams of glycine was introduced in the reactor. Then C9 alkylated di-phenyl amine was introduced.

[0178] In a beaker were charged 70 grams of methanol, 130.6 grams of xylene solvent, and 70 grams of calcium hydroxide. The mixture was stirred for several minutes to obtain a lime slurry.

[0179] To the glass reactor equipped with heating and cooling capability and fitted with a stainless steel mechanical agitator rotating at 350 rpm, a gas inlet tube (2 mm inside diameter) located just above the agitator blades for the addition of CO₂, a distillation column, and condenser was charged the lime slurry. Then 2007.5 grams of alkyl hydroxy benzoic acid (C20 – 24 – branched to 23%) was introduced. The mixture was stirred for 15 min, temperature 40°C. Then 16 grams of glycine was introduced. The reactor was maintained at 43°C for 15 min. Then 835 grams of C9 alkylated di-phenyl amine was introduced in the glass reactor and the stirred mixture was cooled down to 30°C in 15 min. In a beaker were charged 113.8 grams of methanol, 106.8 grams of xylene solvent, 113.8 grams of calcium hydroxide, stirred during few minutes to obtain a lime slurry. The lime slurry was charged to the reactor. Then 56.4 grams of CO₂ were introduced over 59 min at 0.95g/min – temperature increased from 30°C to 40°C. Then the first distillation step started under atmospheric pressure by heating the reactor from 40°C to 65°C in 15 min, then from 65°C to 93°C in 60 min, then from 93°C to 128°C in 30 min. During this step methanol, water and some of meta xylene are boiled off. Then the product is charged in a laboratory centrifuge running at 35000 G to separate insoluble solid products. The liquid part was charged in a 4 liters round bottom reactor, and xylene was distilled by heating the product to 170°C and holding

the product at 170°C during 60 min under 30 millimeters Hg vacuum. Vacuum was broken down with air and cooled down to ambient.

COMPARATIVE EXAMPLES A and B

[0180] Comparative Example A is calcium salicylate (TBN 175) with no amine treatment.

[0181] Comparative Example B is calcium salicylate (TBN 421) with no amine treatment.

[0182] Tables 1-2 summarize the disclosed examples.

[0183] Table 3 summarizes seal test results of Comparative Example A and Examples 3, 9, and 13 in formulated engine oil (grade 15W-40). To ensure proper testing, the samples were formulated contain same TBN level as well as same SOAP content (measurement of organic acid metal salt content).

Table 1

	Comp Ex A	Comp Ex B	Ex 1	Ex 2	Ex 3	Ex 4	Ex 5
Calcium (%)	6.25	13.6	5.86	4.35	4.26	4.48	2.69
BN (ASTM D2896 – mg KOH/g))	175	421	221	123	147	153	112
Sulfated ash (%)	21.2	45.9	19.9	14.8	14.5	15.2	9.1
Sulfated ash/BN	0.1213	0.1090	0.0878	0.1201	0.0984	0.0995	0.0816

	Ex 6	Ex 7	Ex 8	Ex 9	Ex 10	Ex 11	Ex 12	Ex 13
Calcium (%)	3.86	1.81	1.45	2.45	2.05	1.47	2.16	3.86
BN (ASTM D2896 – mg KOH/g)	155	116	159	111	95.2	99.6	100.2	145
Sulfated ash (%)	13.1	6.1	4.9	8.3	7.0	5.0	7.34	13.1
Sulfated ash/BN	0.0845	0.053	0.0310	0.0749	0.0731	0.0454	0.0732	0.0904

	Ex 14	Ex 15	Ex 16	EX 17	Ex 18	Ex 19	Ex 20	Ex 21
Calcium (%)	3.05	4.21	2.2	2.38	1.11	2.53	0.02	2.96
BN (ASTM D2896 – mg KOH/g)	125	159	122	91	44.3	75	33.6	92.6
Sulfated ash (%)	10.4	14.3	7.5	8.1	3.8	8.6	0.1	10.1
Sulfated ash/BN	0.0829	0.0899	0.0612	0.0888	0.0851	0.1146	0.0024	0.1086

	Ex 22	Ex 23	Ex 24	Ex 25	Ex 26	Ex 27	Ex 28	Ex 29	Ex 30
Calcium (%)	2.2	2.51	3.59	5.82	1.29	1.07	12.5	10.6	4.91
BN (ASTM D2896 – mg KOH/g)	--	--	138	214	20.2	93.7	390	307	208
Sulfated ash (%)	7.5	8.5	12.2	19.8	4.4	3.64	35.4	34.3	16.7
Sulfated ash/BN	--	--	0.0884	0.0924	0.2191	0.0388	0.0907	0.1117	0.0802

HTCBT ASTM D6594

[0184] The ASTM D6594 HTCBT test is used to test diesel engine lubricants to determine their tendency to corrode various metals, specifically alloys of lead and copper commonly used in cam followers and bearings. Four metal specimens of copper, lead, tin and phosphor bronze are immersed in a measured amount of engine oil. The oil, at an elevated temperature (170 °C), is blown with air (5 l/h) for a period of time (168 h). When the test is completed, the copper specimen and the stressed oil are examined to detect corrosion and corrosion products, respectively. The concentrations of copper, lead, and tin in the new oil and stressed oil and the respective changes in metal concentrations are reported. To be a pass the concentration of lead should not exceed 120 ppm and the copper 20 ppm.

Table 2

	Comp Ex A	Ex 1	Ex 3	Ex 4	Ex 13
Cu (ppm)	9	14	3	8	4
Sn (ppm)	1	2	1	1	3
Pb (ppm)	11	97	80	56	97

Table 3

	Comp Ex A	Ex 3	Ex 9	Ex 13
Sulfated ash / BN	0.1213	0.0984	0.075	0.0904
Seal test	Fail (cracks)	Pass (no cracks)	Pass (no cracks)	Pass (no cracks)
Seal test variation tensile strength %	Fail (62%)	Pass (42%)	Pass (40%)	Pass (42%)

[0185] For the sake of brevity, only certain ranges are explicitly disclosed herein. However, ranges from any lower limit may be combined with any upper limit to recite a range not explicitly recited, as well as, ranges from any lower limit may be combined with any other lower limit to recite a range not explicitly recited, in the same way, ranges from any upper limit may be combined with any other upper limit to recite a range not explicitly recited. Additionally, within a range includes every point or individual value between its end points even though not explicitly recited. Thus, every point or individual value may serve as its own lower or upper limit combined with any other point or individual value or any other lower or upper limit, to recite a range not explicitly recited.

[0186] Likewise, the term “comprising” is considered synonymous with the term “including.” Likewise whenever a composition, an element or a group of elements is

preceded with the transitional phrase "comprising," it is understood that we also contemplate the same composition or group of elements with transitional phrases "consisting essentially of," "consisting of," "selected from the group of consisting of," or "is" preceding the recitation of the composition, element, or elements and vice versa.

[0187] The terms "a" and "the" as used herein are understood to encompass the plural as well as the singular.

[0188] Various terms have been defined above. To the extent a term used in a claim is not defined above, it should be given the broadest definition persons in the pertinent art have given that term as reflected in at least one printed publication or issued patent. Furthermore, all patents, test procedures, and other documents cited in this application are fully incorporated by reference to the extent such disclosure is not inconsistent with this application and for all jurisdictions in which such incorporation is permitted.

[0189] The foregoing description of the disclosure illustrates and describes the present disclosure. Additionally, the disclosure shows and describes only the preferred embodiments but, as mentioned above, it is to be understood that the disclosure is capable of use in various other combinations, modifications, and environments and is capable of changes or modifications within the scope of the concept as expressed herein, commensurate with the above teachings and/or the skill or knowledge of the relevant art. While the foregoing is directed to embodiments of the present disclosure, other and further embodiments of the disclosure may be devised without departing from the basic scope thereof, and the scope thereof is determined by the claims that follow.

CLAIMS

1. A process for preparing a low ash detergent, the process comprising:
mixing a surfactant composition that includes hydroxybenzoate, sulfonate, or phosphonate detergent with an ashless nitrogen-containing compound to boost the base number of the hydroxybenzoate, sulfonate or phosphonate detergent.
2. The process of claim 1, wherein the mixing occurs in the presence of carbon dioxide or ethylene carbonate.
3. The process of claim 1, wherein the mixing neutralizes the hydroxybenzoate, sulfonate, or phosphonate detergent.
4. The process of claim 1, wherein the hydroxybenzoate, sulfonate, or phosphonate detergent is neutralized by a metal base prior to the mixing or during the mixing.
5. The process of claim 4, wherein the metal base is $\text{Ca}(\text{OH})_2$ or MgO .
6. The process of claim 1, wherein the nitrogen-containing compound is alkylated amine, hydrocarbyl amine, ethyleneamine, aromatic amine, ethanolamine, urea, diphenylamine, alkylated diphenylamine, benzyl amine, piperazine, alkylpiperazine,

dialkylpiperazine, phenoxy amine, benzamide, phenyl amine, phthalimide, or amino acid.

7. The process of claim 1, wherein the nitrogen-containing compound is C₉ diphenylamine, 2-ethylhexyl(tallow)methylamine, ethyl hexyl amine, octylamine, ethylenediamine, N-methylethanolamine, 1,1,-dimethylethylenediamine, 2-methoxyethylamine, di-ethanolamine, N-methylpropylenediamine, tetramethylurea, N-phenyl phenylenediamine, tri-ethylene tetra-amine, tri-ethanol-amine, 1,4-diazabicyclo[2.2.2]octane, N,N'-bis(3-aminopropyl)ethylenediamine, 2-phenoxyethylamine, C₂₀-C₂₄ alkyl-2-phenoxyamine, 2-(2-aminoethoxy) naphthalene, N-(3-(dimethyl amino) propyl) benzamide, phenylpropylamine, N-(2-hydroxyethyl)phthalimide, N-(2-aminoethyl)phthalimide, N-(3-hydroxypropyl) phthalimide, N-(3-aminopropyl) phthalimide, N-(2-(methylamino)ethyl) phthalimide, N-(3-(methylamino)propyl) phthalimide, N-(2-(dimethylamino)ethyl) phthalimide, N-(3-(dimethylamino)propyl) phthalimide, or glycine

8. The process of claim 1, wherein the surfactant is a salt of alkyl hydroxy benzoic acid, alkyl aromatic sulfonic acid, or alkenyl aromatic sulfonic acid.

9. The process of claim 1, wherein the mixing takes place before or after formation of metal carbonate.

10. A process for preparing a low ash detergent, the process comprising:
mixing hydroxybenzoate, sulfonate, or phosphonate detergent with an amine or amine derivative, wherein the amine or amine derivative is added to overbase or boost the base number of the hydroxybenzoate, sulfonate or phosphonate detergent.
11. The process of claim 10, wherein the mixing occurs in the presence of carbon dioxide.
12. The process of claim 10, wherein the mixing neutralizes the hydroxybenzoate, sulfonate, or phosphonate detergent.
13. The process of claim 10, wherein the hydroxybenzoate, sulfonate, or phosphonate detergent is neutralized by a metal base prior to the mixing or during the mixing.
14. The process of claim 13, wherein the metal base is $\text{Ca}(\text{OH})_2$ or MgO .
15. The process of claim 10, wherein the amine or amine-derivative is alkylated amine, hydrocarbyl amine, ethyleneamine, aromatic amine, ethanolamine, urea, diphenylamine, alkylated diphenylamine, benzyl amine, piperazine, alkylpiperazine, dialkylpiperazine, phenoxy amine, benzamide, phenyl amine, phthalimide, or amino acid.

16. The process of claim 10, wherein the amine or amine-derivative is C9 diphenylamine, 2-ethylhexyl(tallow)methylamine, ethyl hexyl amine, octylamine, ethylenediamine, N-methylethanolamine, 1,1,-dimethylethylenediamine, 2-methoxyethylamine, di-ethanolamine, N-methylpropylenediamine, tetramethylurea, N-phenyl phenylenediamine, tri-ethylene tetra-amine, tri-ethanol-amine, 1,4-diazabicyclo[2.2.2]octane, N,N'-bis(3-aminopropyl)ethylenediamine, 2-phenoxyethylamine, C20-C24 alkyl-2-phenoxyamine, 2-(2-aminoethoxy) naphthalene, N-(3-(dimethyl amino) propyl) benzamide, phenylpropylamine, N-(2-hydroxyethyl)phthalimide, N-(2-aminoethyl)phthalimide, N-(3-hydroxypropyl) phthalimide, N-(3-aminopropyl) phthalimide, N-(2-(methylamino)ethyl) phthalimide, N-(3-(methylamino)propyl) phthalimide, N-(2-(dimethylamino)ethyl) phthalimide, N-(3-(dimethylamino)propyl) phthalimide, or glycine.

17. The process of claim 10, wherein the surfactant is a salt of alkyl hydroxy benzoic acid, alkyl aromatic sulfonic acid, or alkenyl aromatic sulfonic acid.

18. The process of claim 10, wherein the mixing takes place before or after formation of metal carbonate.

19. A lubricating oil composition comprising:
major amount of an oil of lubricating viscosity; and

minor amount of a low ash detergent made from a process comprising:

mixing hydroxybenzoate, sulfonate, or phosphonate detergent with an amine or amine derivative, wherein the amine or amine derivative is added to overbase or boost the base number of the hydroxybenzoate, sulfonate or phosphonate detergent.

20. The lubricating oil composition of claim 19, wherein the mixing occurs in the presence of carbon dioxide.

21. The lubricating oil composition of claim 19, wherein the mixing neutralizes the hydroxybenzoate, sulfonate, or phosphonate detergent.

22. The lubricating oil composition of claim 19, wherein the hydroxybenzoate, sulfonate, or phosphonate detergent is neutralized by a metal base prior to the mixing or during the mixing.

23. The lubricating oil composition of claim 19, wherein the metal base is $\text{Ca}(\text{OH})_2$ or MgO .

24. The lubricating oil composition of claim 19, wherein the amine or amine derivative is alkylated amine, hydrocarbyl amine, ethyleneamine, aromatic amine, ethanolamine, urea, diphenylamine, alkylated diphenylamine, benzyl amine,

piperazine, alkylpiperazine, dialkylpiperazine, phenoxy amine, benzamide, phenyl amine, phthalimide, or amino acid.

25. The lubricating oil composition of claim 19, wherein the amine or amine-derivative is C9 diphenylamine, 2-ethylhexyl(tallow)methylamine, ethyl hexyl amine, octylamine, ethylenediamine, N-methylethanolamine, 1,1,-dimethylethylenediamine, 2-methoxyethylamine, di-ethanolamine, N-methylpropylenediamine, tetramethylurea, N-phenyl phenylenediamine, tri-ethylene tetra-amine, tri-ethanol-amine, 1,4-diazabicyclo[2.2.2]octane, N,N'-bis(3-aminopropyl)ethylenediamine, 2-phenoxyethylamine, C20-C24 alkyl-2-phenoxyamine, 2-(2-aminoethoxy) naphthalene, N-(3-(dimethyl amino) propyl) benzamide, phenylpropylamine, N-(2-hydroxyethyl)phthalimide, N-(2-aminoethyl)phthalimide, N-(3-hydroxypropyl)phthalimide, N-(3-aminopropyl) phthalimide, N-(2-(methylamino)ethyl) phthalimide, N-(3-(methylamino)propyl) phthalimide, N-(2-(dimethylamino)ethyl) phthalimide, N-(3-(dimethylamino)propyl) phthalimide, or glycine.

26. The lubricating oil composition of claim 19, wherein the surfactant is a salt of alkyl hydroxy benzoic acid, alkyl aromatic sulfonic acid, or alkenyl aromatic sulfonic acid.

27. The lubricating oil composition of claim 19, wherein the mixing takes place before or after formation of metal carbonate.